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Method of thermically treating a carbonaceous material-  
comprising aqueous fluid and an apparatus therefor

The present invention relates to a method of the thermal treatment of an aqueous fluid comprising carbonaceous material to be gasified, to yield a combustible gas.

5 The gasification of carbonaceous material such as coal in the presence of steam and a limited amount of oxygen has been known in the field for some time. Due to the combustion of a portion of the coal in a suspension of coal in water, the suspension becomes very hot. As a  
10 result, at a temperature of 1000-1200°C and a pressure of approximately 50-100 atmospheres, a carbon monoxide- and hydrogen-comprising combustible gas is produced.

The object of the present invention is to improve the known method and in particular its energy efficiency.  
15 An additional object according to the invention is to improve the control of the thermal treatment.

The method according to the invention comprises the following steps:

20 i) feeding the aqueous fluid comprising carbonaceous material to be gasified to a reactor comprising a course of treatment;

ii) transferring heat to the carbonaceous material-comprising aqueous fluid in counterflow;

25 iii) the gasification of the carbonaceous material in the course of treatment at an elevated temperature in the presence of water, to yield a product stream comprising combustible gas and a carbonaceous material-depleted aqueous fluid; and

30 iv) cooling the product stream until the carbonaceous material-depleted aqueous fluid at least partially comprises a carbonaceous material-depleted aqueous fluid and the separation of the combustible gas from the carbonaceous material-depleted aqueous fluid.

35 This ensures a high conversion of (a continuous stream) carbonaceous material to be gasified into combust-

ible gas, the combustible gas moreover being of very high quality having a high hydrogen content and a low CO-content. Step iii) is carried out under low-oxygen or anoxic conditions. More specifically, no oxygen is added.

5. According to a preferred embodiment the gasification in step ii) is carried out at a temperature and pressure equal to or higher than the critical temperature and pressure of water.

10 At critical conditions complete mixing is realized between the formed combustible gas and water, which ensures good heat transfer to carbonaceous material still to be gasified.

15 In step iii) gasification occurs preferably at a temperature higher than 400°C, in particular at a temperature higher than 500°C.

This ensures a substantially total conversion of all the carbonaceous material initially present.

20 According to a further preferred embodiment the product stream in step iv) is cooled by feeding it in counterflow to the aqueous fluid comprising carbonaceous material to be gasified.

In this manner the temperature of the carbonaceous material-depleted aqueous fluid can be elevated in an energy-efficient fashion.

25 According to an interesting embodiment the carbonaceous material-depleted aqueous fluid is heated, oxygen-comprising gas is introduced into the heated fluid, oxygen is reacted with the carbonaceous material present in the depleted aqueous fluid producing heat, which heat is  
30 transferred to an aqueous fluid comprising carbonaceous material to be gasified.

35 According to this embodiment of the invention, subsequent to the separation of combustible gas, oxygen is supplied to the carbonaceous material-depleted aqueous fluid. This causes carbonaceous material still present in the fluid to be combusted, yielding heat which is utilized to sustain the gasification process. The heat is released at a location where it can be transferred efficiently. Preheating the depleted fluid prior to the addition of

oxygen provides an efficient manner of achieving a very high temperature. This is self-regulating. For instance, insufficient gasification of carbonaceous material at the onset means that more carbonaceous material is left over for oxidation, resulting in the elevation of the temperature, which in turn promotes gasification. Conversely, if too much carbonaceous material is gasified, less carbonaceous material is left over for oxidation and temperature elevations are prevented. If the depleted fluid is heated to above the critical temperature and pressure, the oxygen can easily be mixed completely homogenously with the depleted fluid.

According to a preferred embodiment the combustible gas is combusted in a combustion installation to yield electricity and heat.

In this manner the energy contents of the carbonaceous material to be gasified, which material may be a waste product, is utilized.

According to a very favourable embodiment, a portion of the combustible gas formed is used to attain the elevated temperature described in step ii).

This fuel is available on the spot.

Subsequent heating is effectuated in particular by counterflow to the aqueous fluid comprising carbonaceous material to be gasified.

This provides an efficient utilization of energy.

By the method according to the invention a variety of carbonaceous materials suspended in water can be gasified, such as shredded biomass, coal or peat. An interesting application relates to the gasification of semi-liquid manure and manure suspended in water.

The treatment of semi-liquid manure or manure by the method according to the invention means for one thing the utilization of its energy-content, and for another thing the resolution of problems regarding manure storage, environmental pollution and the spreading of disease.

The invention also relates to an apparatus for the application of the method according to the invention.

A first installation for the thermal treatment of an aqueous fluid comprising carbonaceous material to be gasified to yield a combustible gas and an aqueous fluid poor in carbonaceous material to be gasified comprises a high-pressure pump for feeding under high pressure the aqueous fluid comprising carbonaceous material to be gasified to an elongated tubular reactor having a first and a second end, wherein the first end is provided with an inlet for the aqueous fluid comprising carbonaceous material to be gasified, and the second end is provided with an outlet for the carbonaceous material-depleted aqueous fluid, which reactor is provided in a chamber of an incinerator, which chamber is separated from the lumen of the tubular reactor by means of a heat-conducting reactor wall defining a course of treatment, at the side of the outlet of the tubular reactor the incinerator is provided with a first inlet for oxygen-comprising gas and a second inlet for a fuel, and at the side of the inlet of the reactor the chamber is provided with an exhaust for combustion products, and the exhaust of the reactor is connected to means for the separation of combustible gas formed as a result of gasification, and carbonaceous material-depleted aqueous fluid.

This provides various ways of efficiently utilizing heat energy present in the combustion products. The hot combustion products can be used for the production of steam, and optionally of electricity. It is also possible to fire the incinerator under a pressure of, for instance, 20 bars. It is then possible to utilize the combustion products for the generation of electricity by means of a turbine. In such a case the incinerator is preferably fired utilizing the gas formed by the method under high pressure. The incinerator may be a fluid bed in which the bed material is, for instance, aluminium oxide. This promotes the transfer of heat to the reactor wall. The fuel may be gaseous, liquid or solid. The bed material may comprise a catalyst in order to, for instance, keep the nitrogen emissions low. Alternatively, the incinerator itself may be a reactor in which at high temperatures an

exothermal conversion takes place, yielding a desired product. The preparation of such products may include, for instance, ethane or synthesis gas resulting from the partial oxidation of methane. The gas formed is worked up in a manner known in itself. As source for methane worked up combustibile gas obtained by the method according to the invention may be used.

According to a preferred embodiment, the installation comprises a heat exchanger conducting the carbonaceous material-depleted fluid coming from the tubular reactor in counterflow to the aqueous fluid comprising carbonaceous material to be gasified.

Such an installation is capable of gasifying carbonaceous material in a very energy-efficient manner.

According to a further favourable embodiment the installation comprises a heat exchanger for conducting combustion products coming from the incinerator in counterflow to oxygen-comprising gas to be supplied to the first inlet.

This means that the reactor can reach very high temperatures, so that virtually complete a conversion of carbonaceous material into gas is guaranteed. Further, the very hot combustion gasses leaving the exhaust can be utilized for the production of steam, for instance for the generation of electricity.

In accordance with the invention, an alternative installation for the thermal treatment of an aqueous fluid comprising carbonaceous material to be gasified to yield a combustibile gas and an aqueous fluid poor in carbonaceous material to be gasified, comprises a gasification reactor having a substantially elongated first chamber and a substantially elongated second chamber, the first chamber comprising an inlet opening for the thermal treatment of aqueous fluid comprising carbonaceous material to be gasified, the first chamber and the second chamber being separated by a heat-conducting wall, which heat-conducting wall defines a course of treatment along which, after separation of the combustibile gas, the aqueous fluid comprising carbonaceous material to be gasified is conducted in

counterflow to an aqueous fluid which, as a result of thermal treatment, has become poor in carbonaceous material to be gasified and has been separated from combustible gas, the installation further comprises means for separating the combustible gas and the aqueous fluid which, as a result of thermal treatment, has become poor in carbonaceous material, as well as an exhaust for the combustible gas, further the second chamber is provided with an inlet opening for the supply of compressed oxygen-comprising gas via a pipe and by means of a pumping organ to the aqueous fluid which, as a result of thermal treatment, has become poor in carbonaceous material and which has separated from the combustible gas, and an outlet for a fluid which has been subjected to thermal treatment and oxidation.

Such an installation makes an energy-efficient, self-regulating thermal treatment of fluid comprising carbonaceous material to be gasified possible.

According to a favourable embodiment the means for separating the combustible gas from the aqueous fluid which, as a result of thermal treatment, has become poor in carbonaceous material, comprise a heat exchanger.

This allows a more efficient separation of the combustible gas from the carbonaceous material-depleted aqueous fluid.

Preferably the installation according to the invention comprises means for the combustion of the combustible gas, yielding electricity and heat.

This makes it possible to obtain high-grade energy from waste material which, from an environmental point of view is awkward to dispose of, such as manure but also vegetable, fruit and garden waste, activated sludge, grass cuttings from verges, etc.

According to a further favourable embodiment of the installation according to the invention, the installation further comprises a heat-conducting surface for transferring to at least one chamber heat released during combustion.

According to a preferred embodiment the first chamber surrounds in the longitudinal direction substantially the second chamber and the heat-conducting surface surrounds in the longitudinal direction substantially the first chamber.

Such installations are more energy-efficient.

The invention will now be illustrated by means of the figure legends below and with reference to the appended drawing, in which

Fig. 1 is a schematic illustration of a first installation suitable for carrying out the method in accordance with the invention;

Fig. 2 schematically illustrates a portion of a second installation suitable for carrying out the method in accordance with the invention; and

Fig. 3 is a schematic illustration of a third installation suitable for the application of the method according to the invention.

Reference is now made to Fig. 1, in which a reactor 1 is shown having an inlet 2 for a carbonaceous material-comprising aqueous fluid to be thermally treated. This fluid may be prepared in a vessel 3 into which water ( $H_2O$ ) and a carbonaceous material (C) are introduced. This carbonaceous material may be shredded biomass, coal, manure, etc. By means of a pump 4 a solution or suspension of the carbonaceous material-comprising aqueous fluid to be thermally treated is introduced into the reactor via the inlet 2. The inlet 2 debouches into an elongated first chamber (5) which is separated from a second chamber (7) by a heat-conducting wall (6). In the first chamber (5) at least a portion of the carbonaceous material is gasified yielding a mixture of combustible gas and a carbonaceous material-depleted fluid. In the embodiment shown, this mixture leaves the reactor 1 via outlet 8 and enters a heat exchanger 9, in which the mixture is cooled. This cooling process promotes the separation of combustible gas from carbonaceous material-depleted fluid. In vessel 10 the depleted fluid is separated from the combustible gas. Via a pipe 11, this combustible gas may be transported to an

installation 12, which installation 12 is suitable for the generation of electricity. The installation 12 may comprise a turbine, a combustion engine or, in combination with a reformer for increasing the hydrogen content in the gas, a fuel cell.

The carbonaceous material-depleted fluid from vessel 10 may be heated via the heat exchanger 9 and, with the aid of pump 13, introduced under increased pressure into the second chamber 7.

Via a pump 14 and inlet 15, an oxygen-comprising gas, such as preferably air, is introduced into the second chamber 7. The oxygen reacts with carbonaceous material still present in the depleted fluid, yielding heat. Via the heat-exchanging wall 6, this heat is transferred to the aqueous fluid comprising carbonaceous material to be gasified. It is preferred that in the second chamber near the inlet 15 super critical conditions prevail to allow ready and homogenous mixing of oxygen and carbonaceous material-depleted fluid.

The fact that the energy necessary for gasification is provided by oxidation of the remaining carbonaceous material, affords a highly self-regulatory thermal treatment process.

The liquid that has been subjected to oxidation by oxygen so that, in essence, it no longer comprises any (oxidizable) carbonaceous material, moves in counterflow to the aqueous fluid comprising carbonaceous material to be gasified, thereby efficiently transferring heat. The cooled, essentially carbonaceous material-free fluid leaves the reactor 1 via outlet 16 and flows, in the embodiment shown, into a vessel 17 to separate clean water 18, that may be discharged or used for the preparation of a carbonaceous material-containing aqueous fluid, from inert gasses such as carbon dioxide and possibly nitrogen gas formed during oxidation.

Preferably the carbonaceous material-comprising aqueous fluid to be thermally treated comprises a catalyst to promote the formation of combustible gas. This catalyst may be an ion or a precious metal particle which, if the



clean water from vessel 17 is to be reused for the preparation of suspension, may be allowed to go through the cycle once or several times more, until the clean water contains too many anorganic salts originating from the carbonaceous starting material so that part of, or all the water has to be discharged or improved.

Optionally, the installation according to the invention may also comprise means (not shown) for the utilization of the pressure energy. This may be utilized for the generation of energy or to aid in returning the carbonaceous material-depleted liquid to the reactor 1, more specifically to its second chamber 7. For the return to the second chamber 7 it is, for example, possible to utilize the pressure energy from the gas leaving the vessel 10. Similarly, the pressure energy from the liquid leaving the vessel 17 may also be utilized to relieve the pump 4 or for the generation of electricity.

An alternative embodiment of an installation according to the invention is schematically illustrated in Fig. 2. After the mixture described above has left outlet 8, it is cooled in heat exchanger 9. The heat energy being released is utilized for heating the carbonaceous material-comprising aqueous liquid to be thermally treated in heat exchanger 9'. Advantageously, heat exchanger 9 and 9' are one and the same heat exchanger. The cooled mixture, being highly compressed, may be allowed to expand over a turbine 19 to generate electrical energy. By supplying an oxygen-comprising gas, usually air, the gas may then be combusted. This may be done in a second turbine 20, producing heat and electricity. In the embodiment illustrated, the still hot combustion gasses from turbine 20 are utilized in a heat exchanger, for in counterflow heating of carbon-depleted liquid from vessel 10. With the aid of a pump 22, this liquid is transported to the second chamber 7. Between the vessel 10 and the turbine 19 a heat exchanger 23 may be placed, for heating combustible gas from the vessel 10, which allows a further increase of the pressure and consequently of the performance of turbine 19. The necessary heat is preferably supplied by the

stream leaving the second chamber 7 via heat exchanger 23', which is preferably one and the same as heat exchanger 23.

5. Within the scope of the present invention, the combustion gasses may also be supplied to a further installation for the thermal treatment of a liquid, such as a liquid comprising carbonaceous material to be gasified, which installation possesses a heat-exchanging partition between a first and a second chamber, as well as a heat-exchanging surface for transferring heat from combustion  
10 gas to colder liquid.

According to an important alternative embodiment of the method in accordance with the invention the supply of oxygen is omitted if the gasification takes place at a  
15 temperature and a pressure well above the critical temperature and pressure of water. For this purpose an installation of the kind illustrated in Fig. 3 may be used which has a capacity of 100 MW relating to the energy contents of the carbonaceous material. The installation comprises a high-pressure pump 24 by means of which a sludge  
20 A of shredded biomass, such as wood flour having a solid content of 20%, is transported at a pressure of 30 MPa, via a heat exchanger 25 and an inlet 26 into a tubular reactor 27. The tubular reactor 27 is suitably made of Incoloy 625 and has a (total) length of, for example,  
25 725 m and a surface area of 114 m<sup>2</sup>. The carbonaceous material-depleted stream leaving the reactor 27 via outlet 28 is led through the heat exchanger 25 in counterflow to the sludge A and is optionally cooled further to a temperature of 25°C, for example by using cooling water in  
30 heat exchanger 29. The combustible gas formed in the reactor 27 is separated from the carbonaceous material-depleted stream by means of a gas/liquid separator 30. By lowering the pressure above said depleted stream to, for  
35 example, atmospheric pressure, it is possible to recover more gas from the depleted stream which may be used, for example, for heating the sludge A to be gasified further. The prevailing high pressure makes it advantageous to use a membrane for the separation of hydrogen from the stream.

Via an inlet 31, the remaining gas stream may be fed to an incinerator 32 having a height of 10-15 m, in which the reactor 27 is provided. The incinerator 32 also comprises an inlet 33 for an oxygen-comprising fuel such as air. As shown in Fig. 3, the sludge to be gasified is led in counterflow to the hot gasses released during combustion. In the embodiment shown, the hot gasses leave the incinerator 32 via an exhaust 34 and their energy contents are used for heating air which is to be supplied to the incinerator 32 via inlet 33, by counter-flowing the hot gasses to the air in the heat exchanger 35. A suitable installation is provided with, for example, a heat exchanger 25 having a surface area of 888 m<sup>2</sup> and a heat transfer coefficient of 1200 W/m<sup>2</sup>.K and is fed at a rate of 32 kg dry matter (in 128 kg water) per second. In addition, abstaining from the use of oxygen-comprising air results in the combustible gas having only a low nitrogen content. Partly for that reason, the gas has a high caloric value so that it can be applied more generally. The temperature required for the gasification of the carbonaceous material can be determined quite easily by a person skilled in the art.

In the installation described above, the solid content is suitably at least 10% and preferably at least 20%, such as at least 30%.